Inorganica Chimica Acta, 99 (1985) 195–197

Synthesis of New Cationic Rhodium(I) Complexes with Diolefin and Substituted Quinoline N-Oxides as Ligands

ARISTIDES CHRISTOFIDES and IRENE LABRINOU

Laboratory of Inorganic Chemistry, Aristotelian University of Thessaloniki, Salonica, Greece

Received August 4, 1984

Abstract

The preparations of cationic rhodium(I) complexes of the type $[Rh(COD)L_2]ClO_4$ and $[Rh(COD)L(PPh_3)]ClO_4$ (L = substituted quinoline N-oxides) and the reactions of $[Rh(COD)(4\text{-}MeNO)_2]ClO_4$ with N-, P- and As-donor ligands are described.

Introduction

A number of quinoline and substituted quinoline N-oxide complexes with various metals have been prepared and studied [1]. Quinoline 1-oxide complexes of lanthanide iodides [2] and of cobalt(II) alkanoates [3] have also been prepared.

To our knowledge nothing has been done concerning such rhodium complexes. Uson *et al.* [4] have recently prepared some cationic rhodium complexes by reacting *in situ* substituted pyridine N-oxides with the rhodium complex, $[Rh(COD)(Me_2CO_3)_x]ClO_4$ (COD = 1,5-cyclooctadiene). In an efford to understand the coordination ability of substituted quinoline N-oxides, which are rather bulky ligands, towards rhodium we tried to prepare some complexes by employing a procedure similar to that used by the workers mentioned above [4].

In this paper we report the preparation of cationic rhodium(I) complexes of the type $[Rh(COD)L_2]ClO_4$ and the related mixed-ligand complexes $[Rh(COD)LL']ClO_4$ (L′ = P- or N-donor ligand).

Results and Discussion

The complexes (**I**)–(**III**) were prepared in a similar manner to that employed by Uson *et al.* [4], the differences being the use of a double scale reaction as well as larger volumes of solvents.

The new compounds (complexes (**I**)–(**III**); L = QNO, (**I**); 2-MeQNO (**II**) or 4-MeQNO (**III**) were formed (eqn. 1) as yellow air-stable solids.

$$[Rh(COD)(Me_2CO)_x]ClO_4 + 2L \longrightarrow [Rh(COD)L_2]ClO_4 + XMe_2CO \qquad (1)$$

TABLE I. Analytical Results, Molar Conductivities and Yields for the Complexes $[Rh(COD)L_2]ClO_4$ and $[Rh(COD)LPPh_3]ClO_4$.

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
	C	H	N		
I $[Rh(COD)(QNO)_2]ClO_4$	52.37 (51.97)	4.32 (4.36)	4.62 (4.66)	158	62
II $[Rh(COD)(2\text{-}MeQNO)_2]ClO_4$	53.08 (53.47)	4.84 (4.81)	4.36 (4.46)	178	68
III $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$	53.71 (53.47)	4.86 (4.81)	4.56 (4.46)	163	80
IV $[Rh(COD)(QNO)(PPh_3)]ClO_4$	57.98 (58.55)	4.73 (4.77)	2.25 (1.95)	171	50
V $[Rh(COD)(2\text{-}MeQNO)(PPh_3)]ClO_4$	58.60 (59.06)	5.07 (4.96)	2.15 (1.91)	148	80
VI $[Rh(COD)(4\text{-}MeQNO)(PPh_3)]ClO_4$	58.98 (59.06)	4.89 (4.96)	2.36 (1.91)	140	86

0020-1693/85/$3.30

TABLE II. IR Data for the Cationic Complexes (cm^{-1}).

L	Ligand[a] ν(NO)	$[Rh(COD)L_2]ClO_4$		$[Rh(COD)L(PPh_3)]ClO_4$	
		ν(NO)	$\Delta\nu$(NO)[b]	ν(NO)	$\Delta\nu$(NO)[b]
QNO	1240, 1220	1223, 1205	16	1215, 1200	15
4-MeQNO	1236, 1206	1208, 1168	33	1208, 1162	36
2-MeQNO	1204	1188	16	1181	23

[a] Data from ref. [1] in connection with recorded spectra of pure ligands. [b] $\Delta\nu$(NO) = ν(NO) (ligand) – ν(NO) (complex).

In order to prepare complexes incorporating quinoline-N-oxides bearing electron withdrawing substituents, we tried the reactions with 4-ClQNO, 4-NO_2QNO and 2-PhQNO, but they either do not react or they give decomposition products.

Addition of stoichiometric amounts (1/1) of triphenylphosphine to dichloromethane solutions of complexes **(I)**–**(III)** results in displacement of one mol of quinoline N-oxides and formation of light-brown mixed complexes **(IV)**–**(VI)**. Analytical results, conductivities, and yields for complexes **(I)**–**(VI)** are given in Table I.

The ^{31}P NMR spectra of the above compounds taken in deuterated chloroform indicate that they undergo decomposition to some extent in solution. However, all the spectra show double resonances at *ca.* 26.9 ppm with rhodium–phosphorous coupling of *ca.* 151 Hz. The observed chemical shifts are very close to those reported for similar complexes [5, 6].

The complex **(III)** reacts with 4-aminopyridine in 1/1 molar ratio afferding the novel mixed complex $[Rh(COD)(4\text{-}MeQNO)(4\text{-}NH_2Py)]ClO_4$. The same complex reacts similarly with 1,10-phenanthroline displacing the 4-MeQNO and forming the complex $[Rh(COD)Phen]ClO_4$ previously reported [7].

The conductance data of the complexes **(I)**–**(VI)** suggest the presence of 1:1 electrolytes in acetone, indicating non-coordinated anions in this solvent. Furthermore, the molar conductivity of the complex **(I)** in nitrobenzene also leads to the same conclusion [8].

IR Spectra

All the studied complexes show the characteristic bands of the uncoordinated anion ClO_4^-(Td) [9] at 1090 (ν_3) and 620 (ν_4) cm^{-1}, along with the absorptions of all the coordinated ligands.

The values of ν(N–O) for the free and the coordinated ligands along with the corresponding $\Delta\nu$(N–O) are given in Table II. Upon complexation the ν(N–O) is shifted towards lower wavenumbers than those of the free ligands. Bands due to δ(N–O) around 800 cm^{-1} do not exhibit appreciable shifting, as it was shown earlier in the case of substituted pyridine N-oxides analogues [4]. Weak peaks in the 500–360 cm^{-1} region could be assigned to ν(Rh–O) [4, 10].

Experimental

C, H and N analyses were done with a Perkin-Elmer 240 microanalyzer. Infrared spectra were recorded with Nujol mulls or KBr discs on a Perkin-Elmer 467 spectrophotometer (over the range 4000–200 cm^{-1}).

Conductivities were measured in *ca.* 5×10^{-4} M acetone solutions with a Industrial Conductivity Bridge RC 216 B2. The ^{31}P NMR spectra were recorded on JEOL PFT spectrometer using $CDCl_3$ solutions. $[RhCl(COD)]_2$ was prepared according to published methods [11]. Quinoline N-oxide and its derivatives were prepared by literature methods [12–14] and recrystallized prior to use. All reactions were performed at room temperature in air.

Preparation of Complexes of the type $[Rh(COD)L_2]ClO_4$ (I–III)

All these were prepared in a similar way, and the following example is representative.

To a solution of $[Rh(COD)(Me_2CO)_x]ClO_4$, obtained by treating $[RhCl(COD)]_2$ (0.099 g, 0.2 mmol) with $AgClO_4$ (0.083 g, 0.4 mmol) in 80 ml of acetone and after the removal of the precipitated AgCl, quinoline N-oxide (0.144 g, 0.8 mmol) was added under constant stirring (0.5 h). The solution changed rapidly colour to intense yellow. It was then concentrated under vacuum to a small volume (*ca.* 10 ml) giving a residue, which was washed with diethyl ether (2×5 ml) affording yellow microcrystals of $[Rh(COD)(QNO)_2]ClO_4$ **(I)** (0.170), which were dried *in vacuo*.

Preparation of Complexes of the type $[Rh(COD)L(PPh_3)]ClO_4$ (IV–VI)

All these were prepared in a similar manner, and the following example is representative.

Complex **(III)** (0.125 g, 0.2 mmol) in dichloromethane (20 cm^3) was treated with triphenylphosphine (0.0524 g, 0.2 mmol). The mixture was stirred for 0.5 h to give a cloudy solution, which was filtered. The filtrate was concentrated to a small volume (*ca.* 3 cm^3) and diethylether (3 cm^3) was added. The solution became cloudy again and the stirring was continued for a while to help the formation of the crystals. Cooling to –5 °C afforded light-brown crystals of $[Rh(COD)(4\text{-}MeQNO)(PPh_3)]ClO_4$ (**VI**) (0.127 g), which was dried *in vacuo*.

The ^{31}P NMR spectrum in $\{^2H_1\}$ chloroform showed double resonances at 27.3 [$J(RhP)$ = 152 Hz]. The complexes (**IV**) and (**V**) also showed double resonances at 27.0 [$J(RhP)$ = 151 Hz] and 26.6 [$J(RhP)$ = 150 Hz)], respectively.

Reactions of [Rh(COD)(4-MeQNO)₂] ClO₄

(i) Addition of 0.1 mmol of 4-aminopyridine to an acetone solution (12 cm^3) of the starting complex (0.1 mmol) gave a yellow solution, which after addition of diethylether and stirring for 1 h gave yellow crystals of $[Rh(COD)(4\text{-}MeQNO)(4\text{-}NH_2Py)]ClO_4$. *Anal.* Found: C, 49.15; H, 4.78; N, 6.97. $C_{23}H_{27}N_3O_5ClRh$ calcd.: C, 48.99; H, 4.83; N, 7.45%. IR: $\nu_{max}(N{-}O)$ 1204s, 1149s and $\nu(ClO_4^-)$ 1084 vs, 607s.

(ii) Addition of phen (0.1 mmol) to acetone solution of 0.1 mmol of $[Rh(COD)(4\text{-}MeQNO)_2]ClO_4$ resulted in a rapid change in colour from yellow to red, and gave red microcrystals of $[Rh(COD)(Phen)]ClO_4$ [7].

Acknowledgement

We thank Dr. Martin Murray, University of Bristol (England), for recording the ^{31}P NMR spectra.

References

1 N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973).

2 L. Ramakrishnan and S. Soundararajan, *Rev. Roum. Chim., 22,* 395 (1977); *Chem. Abstr., 86,* 182262t (1977).

3 N. Kumar, P. Kachroo and R. Kant, *Transition Met. Chem., 4,* 315 (1979); *Chem. Abstr., 92,* 51156n (1980).

4 R. Uson, L. A. Oro, M. A. Ciriano and F. Lahoz, *J. Organomet. Chem., 217,* 251 (1981).

5 R. Uson, L. A. Oro, M. A. Ciriano, F. J. Lahoz and M. C. Bello, *J. Organomet. Chem., 234,* 205 (1982).

6 R. Uson, L. A. Oro, M. A. Ciriano and F. J. Lahoz, *J. Organomet. Chem., 240,* 429 (1982).

7 C. Cocevar, G. Mestroni and A. Camus, *J. Organomet. Chem., 35,* 389 (1972).

8 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

9 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961).

10 G. B. R. James, R. H. Morris and K. J. Reiner, *Can. J. Chem., 55,* 2353 (1977).

11 R. B. King, 'Organometallic Syntheses', Academic Press, New York - London, 1965.

12 E. Ochiai, 'Aromatic Amine Oxides', Elsevier, Amsterdam, 1967.

13 E. Ochiai, *J. Org. Chem., 18,* 534 (1953).

14 T. Kato and H. Yamanako, *J. Org. Chem., 30,* 910 (1960).